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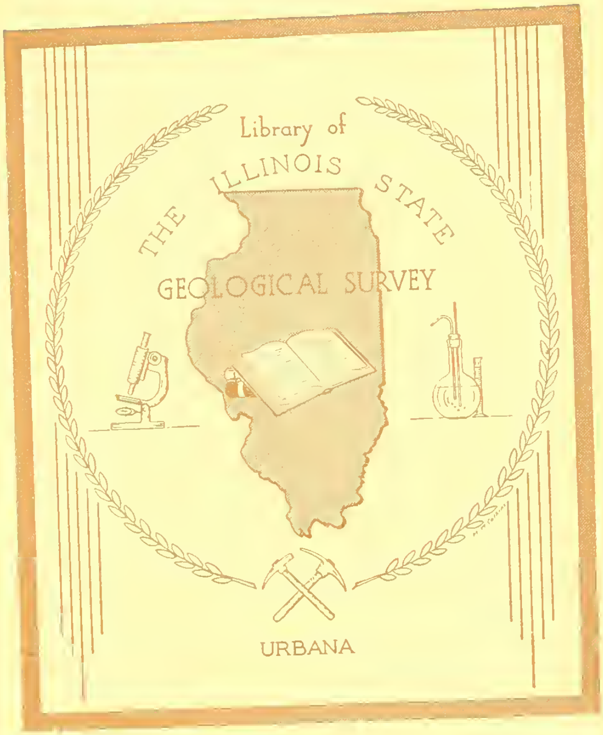
Jack A. Simon, Chief • Urbana, IL 61801



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ATTENUATION OF POLLUTANTS IN MUNICIPAL LANDFILL LEACHATE BY CLAY MINERALS

Part 1—Column Leaching and Field Verification

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ABSTRACT

To evaluate the potential of clay minerals for attenuating the various chemical constituents of landfill leachate, leachate was collected by anaerobic techniques from the 15-year-old Du Page County sanitary landfill near Chicago and passed through laboratory columns that contained mixtures of calcium-saturated clays and washed quartz sand in various percentages. The columns simulated the slow, saturated, anaerobic flow of leachate through earth materials outside the landfill. Manometers were placed in each column to measure any changes in permeability. Leachates were run through the columns for periods of up to 10 months, during which time effluents were periodically collected and analyzed for 16 chemical constituents. The column contents were then cut into sections and analyzed to determine the vertical distribution of chemical constituents in each column.

Chloride, sodium, and water-soluble organic compounds (COD) were relatively unattenuated by passage through the columns of clay; potassium, ammonium, magnesium, silicon, and iron were moderately attenuated; and the metals lead, cadmium, mercury, and zinc were strongly attenuated by even small amounts of clay. Concentrations of calcium, boron, and manganese were markedly higher in the effluents than in the original leachate.

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* Present address: Ontario Ministry of the Environment, Toronto, Canada.

Of the three clays used in the study, montmorillonite had the highest attenuation capability, followed by illite and then kaolinite. The principal attenuation mechanism for the metals Pb, Cd, Hg, and Zn was found to be precipitation. The metals accumulated in the surface layers of the columns.

The results of the column leaching experiments were checked against detailed data on actual conditions at landfills. A "hardness halo" at the landfill sites corresponded to the Ca release observed in the column experiments. The relative attenuation rates of some of the ions were also confirmed by the field data.

Leachate reduced the hydraulic conductivity of the columns during the laboratory experiments. A similar change in hydraulic conductivity was not clearly shown in the field data but probably exists.

A ranking system was developed for evaluating the relative pollution hazard for municipal leachates. The new ranking method overcomes the problems found in a method for rating hazardous wastes that was previously proposed to the U.S. Environmental Protection Agency.

The results of the study suggest that over-all pollution from landfill leachate would be reduced if landfill liners of earth materials were designed for higher hydraulic conductivity. Properly designed liners would selectively attenuate the toxic pollutants from the leachate and allow the ground water to dilute the nontoxic components that can be tolerated without harmful effects at much higher concentrations.

INTRODUCTION

During the past 30 years, the landfill method for disposal of municipal and industrial waste has been widely used in the United States. Some 14,000 landfills across the country accommodate more than 90 percent of our nation's wastes (Garland and Mosher, 1975). These landfills accept more than 360 million tons of household, commercial, industrial, and municipal solid waste per day, at a cost to the public of more than 4.5 billion dollars annually (Black et al., 1968).

As industry in the United States complies with the Clean Air Act and the Federal Water Pollution Control Act, the volume of solid wastes, sludges, and liquid concentrates of pollutants from industry is expected to double in the next 10 years. The disposal of such huge volumes of solid waste in landfills is not without its environmental impact. When refuse buried in a landfill comes in contact with water, leachate—a mineralized liquid with a high content of organic substances—is produced that may move out of the fill and pollute the ground water.

Garland and Mosher (1975) cited several examples of such pollution, and Apgar and Satterthwaite (1975) gave an example of severe economic damage incurred when a drinking-water aquifer was polluted by leachate from a landfill in New Castle County, Delaware. Leachate from the landfill migrated more than 800 feet and contaminated the Potomac aquifer 4 years after the landfill site had been closed. Levels of organic compounds and metal ions in the water were so high that it was no longer potable. The county was reported to have spent $800,000 for interim solutions, and, if the dump must be moved to completely remedy the situation, the cost reportedly may go as high as 20 million dollars. In addition to the monetary costs, the county estimates that it will take 10 years to restore the aquifer to full use.

In another case, reported by Garland and Mosher (1975), contamination of ground water by selenium was found to extend more than 2 miles from a dump site in Long Island. As was true in this case, contamination by metals may impart no odor or color to indicate that the water is polluted.

The solid waste problem is most acute in metropolitan areas, where competition for the available land is intense. A city of 2 million inhabitants generates 5000 tons of solid waste per day (Wirenius and Sloan, 1973), which rapidly fills the convenient landfill locations. The problem of finding environmentally acceptable sites close to the metropolitan area is compounded by urban sprawl and persistent opposition from citizen and environmental groups. The rapid increase in problems and costs associated with transporting refuse for long distances now make it prudent to consider sites that were previously unacceptable because they failed to meet certain geologic and hydrologic criteria.

In January 1975, Illinois had 2040 waste disposal sites recorded with the Illinois State Environmental Protection Agency. The management of refuse disposal in Illinois has greatly improved since 1965, when the Illinois Refuse Disposal Act was passed. The act assigned the regulation of solid waste disposal to the Department of Public Health. More comprehensive regulation was provided in 1970 with the creation of the Illinois Environmental Protection Agency. Regulations were passed that were designed to insure that solid waste disposal facilities are located at such sites and operated in such a manner that the physical environment and public health are protected. These regulations have been enforced for the past 10 years, during which time the Illinois State Geological Survey has assisted the regulatory agencies by evaluating the hydrogeologic conditions at proposed or operating waste disposal sites. Pollution hazards at about 100 sites per year have been appraised by the Survey in the past 8 years. Some sites were not approved for geologic reasons—locations in floodplains or gravel pits, on fractured rock over aquifers, on steep grades, or in areas of special historical or environmental significance. Other sites were approved but never put into operation, most of them because of persistent opposition from citizen and environmental groups.

The future of landfill disposal is clear. Acceptable disposal sites will be difficult to find, their location will be approved only after certain geologic and hydrologic criteria are met, and greater care will be required in their operation. The relative unavailability of geologically acceptable sites close to metropolitan areas and the rapidly escalating costs associated with transportation of waste materials across long distances now make it economically feasible to consider physical modification of geologically unacceptable sites that may be ideal in other respects. The Illinois Geological Survey has conducted, at several landfill sites in northeastern Illinois (Hughes, Landon, and Farvolden, 1971), extensive studies of the movement of pollutants through various geologic strata and in a variety of hydrologic settings. Cartwright and McComas (1968) conducted geophysical investigations at the same sites. These studies, and others by Apgar and Langmuir (1971) and Emrich (1972), have indicated that pollutants in leachate can be detected at various distances from a landfill, depending on the soil's clay content or the hydraulic conductivity of the soil strata. It has therefore been suggested that a clay liner in the bottom of such previously unacceptable sites as gravel pits or old quarries could make them acceptable as depositories of municipal and/or industrial wastes. However, no sound evidence existed to indicate how thick such a layer must be or what types of clay minerals are best suited for removal of pollutants from municipal leachate.

To investigate and evaluate the attenuating properties of clay minerals used as liners (natural or artificial) for sanitary landfills, we conducted a laboratory study related to the Geological Survey's ongoing field program of evaluation and research in sanitary landfills. This report relates what was observed around sanitary landfills to two phenomena noted in the laboratory—the elution of large amounts of the calcium ion from the laboratory columns and the reduction in hydraulic conductivity that resulted from the introduction of leachate to the clay-sand mixtures.

There is little doubt that municipal leachates are noxious waste streams that pose a potential threat to public health (Peterson, 1974). To assess the magnitude of their pollution hazard is difficult and was the subject of the U.S. EPA (1973a) decision model for selecting, screening, and ranking hazardous wastes streams. Use of the decision model's priority ranking formula requires evaluation of the "critical product" (pollution hazard). As no actual waste-stream data were available for municipal landfill leachates, one goal of this study was to provide such data for use in determining the mobility index of several major pollutants found in municipal leachates that had passed through simulated clay mineral landfill liners. The mobility index could then be used to compute the pollution hazard for most of the chemical constituents found in municipal leachate.

The laboratory results make it possible to estimate the amounts of clay required to attenuate leachate as it passes through clay materials. The results can also be applied to the land disposal of industrial wastes.

Acknowledgments

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EXPERIMENTAL

Materials

The clays used in this study were the purified clay minerals kaolinite (1:1 lattice type), montmorillonite (2:1 expanding lattice), and illite (2:1 nonexpanding lattice, mica type). These particular clay minerals were chosen because they are the most common clay minerals in earth materials that would be used, separately or combined, for landfill sites. Earth materials containing one or more of these clay minerals can generally be obtained locally.

The clays were brought to the laboratory, where they were crushed, ground, and subjected to sedimentation to obtain the < 2 μm particle fraction that contained essentially pure clay minerals. The clays were saturated with Ca. The results of chemical analyses of the three clay minerals are given in table 1. (Details of the methods used and results of X-ray diffraction analyses of the clays were given by Griffin and Shimp, 1976.) The predominantly Ca-saturated, < 2 μm fractions of the clays were then used in the column leaching studies.

The leachate used was collected from the Du Page County landfill (well MM 63). The details of the site description and well location were given by Hughes et al. (1971). The leachate was collected by using a tubing pump and large plastic containers that were equipped with valves to allow continuous purging with argon gas to maintain anaerobic conditions.

The leachate was stored under argon in two 53-gallon plastic closed-head drums. One drum was taken to the Argonne National Laboratories and sterilized by gamma-ray irradiation from a cobalt source that gave a dose of 3.36×10^6 rad at the center of the drum. Both the sterile and natural drums were refrigerated at a constant temperature of 3° to 5° C. Argon was introduced over the top of the leachate in the drum containing the microbially active leachate, while a gas mixture of 12 percent ethylene oxide and 88 percent freon was introduced over the sterilized leachate to maintain both sterility and an anaerobic environment. Mercuric nitrate salt was later added to that drum (table 2) to insure continued sterility. To determine whether sterility had been achieved, plate counts were made on the leachate of both drums by using potato dextrose agar media. No growth occurred on plates innoculated with the sterilized leachate, but active growth of microbial colonies was observed on plates innoculated with the natural leachate.

The results of chemical analysis of the leachates are presented in table 2. (Chemical procedures used were given by Griffin and Shimp, 1976.) For comparison, table 2 also summarizes the range of leachate characteristics found for more than 20 other leachates given by Garland and Mosher (1975). The Du Page leachate is approximately 15 years old and has a lower total salt, phosphate, and sulfate content than many of the others. In addition, the

TABLE 1—CHEMICAL ANALYSES OF CLAY MINERALS USED IN ATTENUATION STUDIES OF LEACHATE POLLUTANTS

Element	Kaolinite* (ppm)		Montmorillonite† (ppm)		Illite‡ (ppm)	
	Exchangeable	Total	Exchangeable	Total	Exchangeable	Total
Calcium	2,592.	3,700	13,120.	22,300	5,248.	23,350
Magnesium	76.8	1,800	680.	25,500	800.	10,430
Sodium	43.2	929	24.0	178	115.2	1,050
Potassium	87.2	8,200	240.	1,100	800.	56,270
Ammonium	13.0	40	43.	38	50.	62.5
Iron	< 2.0	6,600	< 2.0	25,500	< 2.0	28,730
Manganese	0.06	29	0.02	25	0.37	< 390
Lead	< 2.0	46	< 2.0	< 15	< 2.0	93.8
Cadmium	< 0.2	< 3	< 0.2	< 3	< 0.3	18.8
Zinc	0.80	20	1.00	40	2.5	37.5
Boron	—	46	—	3	—	43.8
Aluminum	—	221,800	—	95,600	—	130,100
Silicon	—	217,700	—	284,800	—	226,500
Titanium	—	14,700	—	1,300	—	4,010
Total carbon (%)		0.54		0.93		2.19
Organic carbon (%)		0.51		0.92		1.81
Inorganic carbon (%)		0.03		0.01		0.38
Cation exchange capacity (CEC) (meq/100 g)		15.1		79.5		20.5
Surface area (m^2/g)		34.2		86.0		64.6

* From Pike County, Illinois.

† Southern bentonite from American Colloid Company.

‡ From Minerva Company mine, Illinois.

organic matter of the Du Page leachate consists mainly of microbially resistant compounds, which have been found to be more mobile in soils than biodegradable compounds (Hughes, Landon, and Farvolden, 1971; Gowler, 1973).

Apparatus

The laboratory apparatus used in the leaching study consisted of laboratory columns containing various mixtures of clay minerals and washed quartz sand through which leachate was passed (fig. 1). The columns and apparatus were constructed to simulate the slow (< 2 pore volumes per month), saturated, anaerobic flow of leachate that is thought to occur at the bottom of a landfill. The entire column leaching system was kept under argon to maintain anaerobic conditions. A tubing pump lifted the leachate to a 5-gallon plastic carboy that acted as both a constant-head device (Marriot bottle) and a temperature equilibration reservoir. The leachate was passed through

TABLE 2—CHEMICAL CHARACTERISTICS OF LANDFILL LEACHATES

Component	Range of all values given by Garland and Mosher (1975) (mg/l)	Du Page leachate used in column study (mg/l)	
		Natural	Sterile
Chemical oxygen demand (COD)	40 - 89,520	1,340.	10,603.*
Biological oxygen demand (BOD)	9 - 54,610	—	—
Total organic carbon	256 - 28,000	—	—
Organic acids	—	333.	290.
Carbonyls as acetophenone	—	57.6	90.1
Carbohydrates as dextrose	—	12.	11.
pH	4 - 9	6.9	7.2
Eh (oxidation potential) (mv)	—	+7.	+75.
Total dissolved solids	0 - 42,276	5,120	5,280
Electrical conductivity (mmhos/cm)	3 - 17	10.20	10.42
Alkalinity ($CaCO_3$)	0 - 20,850	—	—
Hardness ($CaCO_3$)	0 - 22,800	—	—
Total phosphorus	0 - 154	0.1	0.1
Ortho-phosphate	6 - 85	—	—
NH_4-nitrogen	0 - 1,106	862.	773.
NO_3+NO_2-nitrogen	0 - 1,300	—	—
Aluminum	—	0.1	0.1
Arsenic	—	0.11	0.14
Boron	—	29.9	28.5
Calcium	5 - 4,080	46.8	43.2
Chloride	34 - 2,800	3,484.	3,311.
Sodium	0 - 7,700	748.	744.
Potassium	3 - 3,770	501.	491.
Sulfate	1 - 1,826	0.01	0.01
Manganese	0 - 1,400	0.1	0.1
Magnesium	16 - 15,600	233.	230.
Iron	0 - 5,500	4.2	3.0
Chromium	—	0.1	0.1
Mercury	—	0.0008	0.87*
Nickel	—	0.3	0.3
Silicon	—	14.9	15.0
Zinc	0 - 1,000	18.8	16.3
Copper	0 - 10	0.1	0.1
Cadmium	0 - 17	1.95	1.88
Lead	0 - 5	4.46	4.26

* Added as a result of sterilization maintenance.

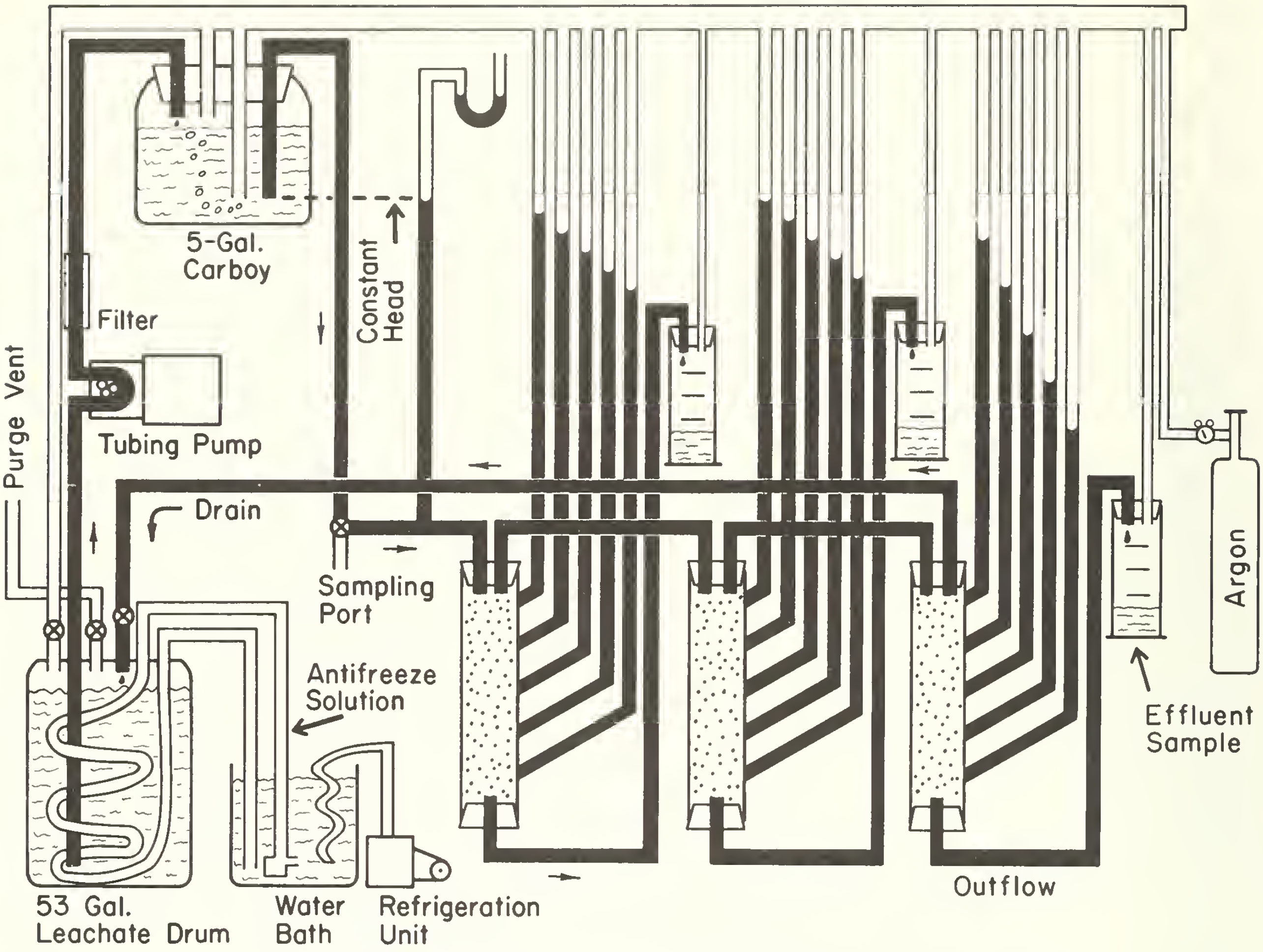

Fig. 1 - Diagram of column apparatus used in leachate study.

the columns and the effluents were collected in graduated cylinders, which also allowed measurement of the flow rates. The outflow tube was kept above the top of the columns to insure saturated flow, the level being moved either up or down to keep the flow rates relatively constant throughout the experiment.

The columns were constructed of acrylic tubing 2 inches in diameter. Along each column five manometer outlets were fitted. To simulate field conditions the leachate containers and columns were either painted black or masked with black tape to prevent growth of organisms, such as algae or photosynthetic bacteria, which are not indigenous to deep refuse leachate.

Procedure

The sand grains were coated with the clays, according to methods given by Grim and Cuthbert (1945). The clay minerals and sand were then uniformly packed in the columns to a depth of 40 cm, except for the 32 percent and 64 percent montmorillonite columns, which were 30 cm deep. The columns were packed to bulk densities approximating those of naturally occurring glacial tills (∿ 1.8 g/cc; Manger, 1963).

TABLE 3—PHYSICAL AND CHEMICAL PROPERTIES OF THE COLUMN CONTENTS

Column content (%)	Cation exchange capacity (meq/100 g)		Bulk density (g/cc)		Initial hydraulic conductivity (cm/sec)	
	Set A*	Set B†	Set A	Set B	Set A	Set B
100 Sand	0.0	.1	1.71	1.71	$1.27.10^{-3}$	$1.80.10^{-3}$
2 Montmorillonite	1.4	2.3	1.71	1.72	$9.45.10^{-4}$	$7.93.10^{-4}$
4 Montmorillonite	3.2	4.3	1.77	1.74	$4.34.10^{-4}$	$3.47.10^{-4}$
8 Montmorillonite	7.3	7.2	1.79	1.78	$4.70.10^{-4}$	$2.61.10^{-4}$
16 Montmorillonite	11.9	12.1	1.87	1.86	$1.22.10^{-5}$	$1.44.10^{-5}$
32 Montmorillonite	26.8	24.0	1.55	1.52	$1.27.10^{-6}$	$2.17.10^{-6}$
64 Montmorillonite	56.2	55.5	1.23	1.11	$3.05.10^{-7}$	$6.83.10^{-7}$
2 Kaolinite	0.7	0.4	1.68	1.70	$7.44.10^{-4}$	$4.53.10^{-4}$
4 Kaolinite	1.1	0.8	1.76	1.74	$4.78.10^{-5}$	$2.76.10^{-5}$
8 Kaolinite	1.5	1.4	1.80	1.77	$9.90.10^{-4}$	$8.25.10^{-4}$
16 Kaolinite	1.8	2.5	1.87	1.90	$2.86.10^{-5}$	$1.92.10^{-6}$
32 Kaolinite	3.8	3.4	1.66	1.55	$2.40.10^{-6}$	$4.81.10^{-6}$
64 Kaolinite	9.6	8.5	1.22	1.32	$5.45.10^{-7}$	$4.57.10^{-7}$
4 Illite	0.8	0.9	1.80	1.81	$8.17.10^{-4}$	$7.16.10^{-4}$
16 Illite	3.5	3.2	1.83	1.91	$2.68.10^{-5}$	$2.19.10^{-5}$
8K + 8I	2.4	2.3	1.90	1.98	$1.48.10^{-6}$	$1.68.10^{-6}$
8M + 8K + 8I	8.8	8.5	1.64	1.69	$8.08.10^{-6}$	$9.43.10^{-6}$

* Natural leachate.

† Sterile leachate.

Table 3 gives chemical and physical properties of the column contents. The hydraulic conductivities for each amount of clay and bulk density agree with those given by Todd (1959) for natural materials. Table 3 also gives the percentages of clay minerals in each column. Pure quartz sand was added to make a total of 100 percent. A complete geometric progression of clay percentages, from 2 percent to 64 percent kaolinite and montmorillonite, and two mixtures of clays were tested. A 100 percent sand column also was included, but only 4 percent and 16 percent quantities of illite were included because kaolinite and illite have very similar cation-exchange and lattice-expansion properties, making a complete geometric array for illite unnecessary.

After the characteristics of the leachate and the column contents were determined, the leachate was passed through the columns for periods of between 6 and 10 months, depending on the hydraulic conductivity in the individual column. The hydraulic conductivity (K) was computed by the formula:

$$K = \frac{QdL}{AdH}$$

where Q = flow rate in cm^3/sec,
A = cross sectional area of column in cm^2,
dL = length of the column in cm, and
dH = head of water in cm.

During the leaching, effluents from each column were collected periodically, and measurements were made for Na, K, Ca, Mg, Al, Zn, Pb, Cd, Hg, Fe, Mn, NH_4, B, Si, Cl, chemical oxygen demand (COD), Eh, pH, and hydraulic conductivity. Finally, after the leaching of approximately 15 pore volumes, the clay mineral columns were cut into sections and the contents analyzed to determine the vertical distribution of chemical constituents in each column.

Duplicate sets of columns were used in the experiment; one set of columns was leached with natural effluent, while the second was leached with sterilized effluent. The sterilized treatment was used to determine how gross biological activity might affect hydraulic conductivity of leachate through clay minerals used as liners. The results of the experiment were analyzed statistically by using the paired t statistic to determine whether the attenuation of the chemical constituent by sterile leachate was significantly different from the attenuation by natural leachate and whether each clay mineral produced different results. Linear regression analysis and moving average analysis also were performed on the column effluent data tc determine the relation between hydraulic conductivity, attenuation, and clay mineral properties.

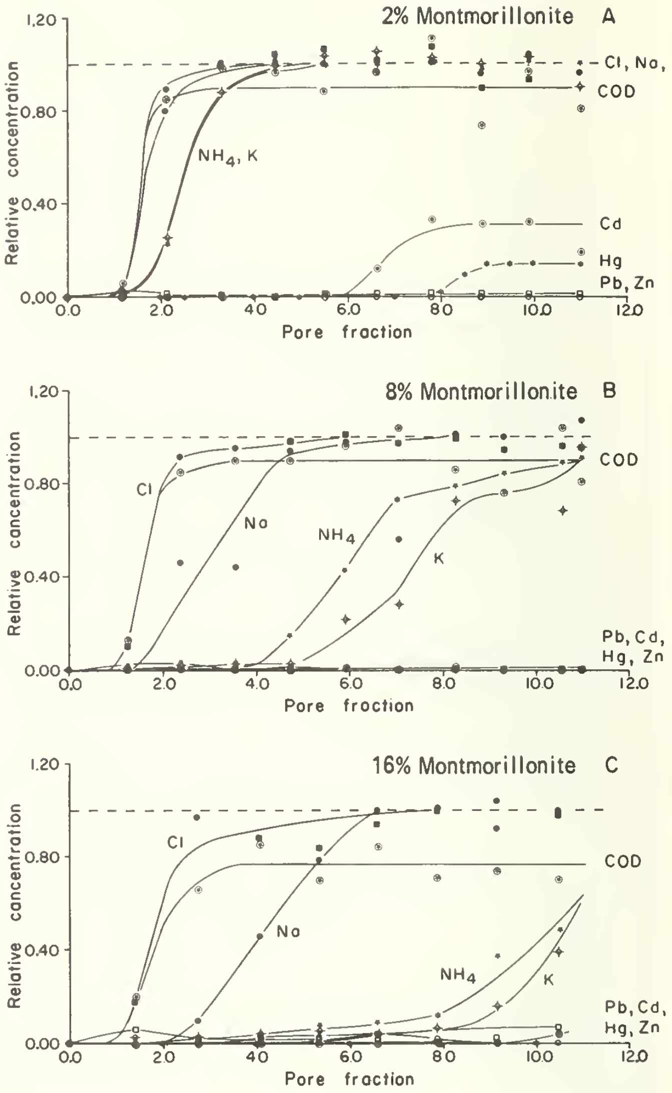

Fig. 2 - Relative concentrations of column effluents for several elements, shown as a function of pore fraction of leachate passed through columns containing different percentages of montmorillonite.

COLUMN LEACHING STUDIES

Attenuation of Effluent Constituents

Results of analyses of several representative column effluents are shown in figures 2 and 3, plotted as relative concentration versus pore fraction. Relative concentration is the ratio of the column effluent concentration divided by the influent concentration. Thus the "breakthrough" point for

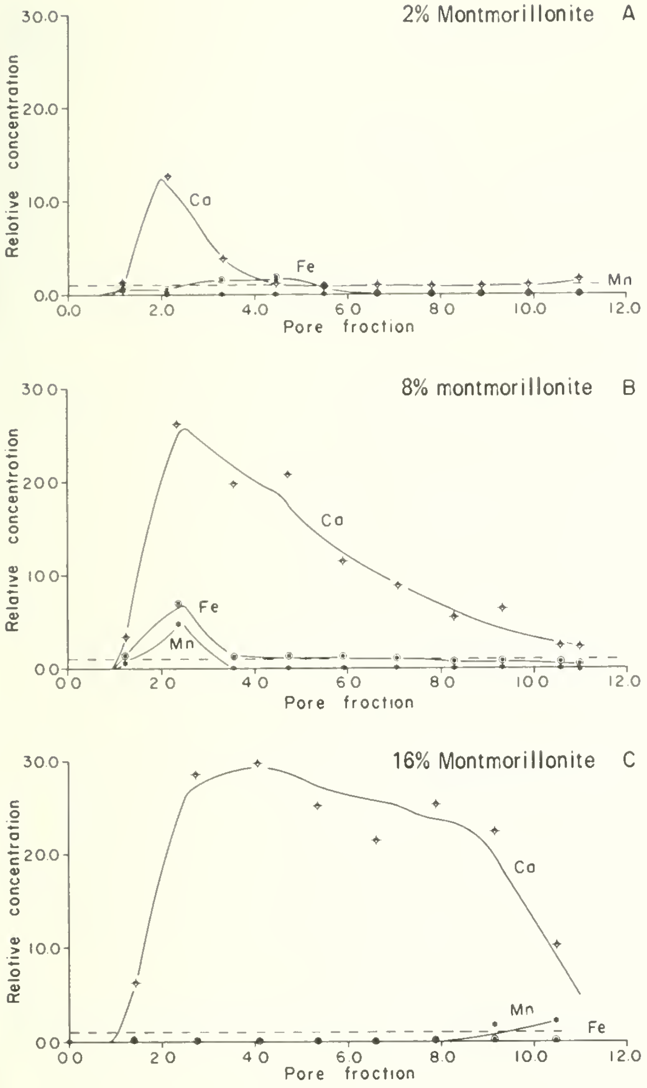

Fig. 3 - Relative concentrations of column effluents for calcium, iron, and magnesium, shown as a function of pore fraction of leachate passed through columns containing different percentages of montmorillonite.

a given element is where the column effluent concentration equals half the influent concentration and has a value of 0.5. A pore volume of effluent is defined as the volume necessary to displace the volume of interstitial liquid in the pore spaces in the column. The pore fraction is then given as the cumulative volume of column effluent divided by the pore volume of the individual column.

Figures 2 and 3 illustrate the wide range of attenuation observed for several elements contained in the leachate as it passed through columns containing 2, 8, and 16 percent montmorillonite clay. The amount of reduction in concentration of a given element as it passes through the columns is reflected by the shift of the curves toward higher pore volumes. The results in figure 2 for Cl, Na, NH_4, and K are qualitatively in excellent agreement with the results reported by Farquhar and Rovers (1975), who used soils in their tests. The attenuation order also follows the general order of cation replaceability given by Grim (1968).

Figure 3 shows the negative attenuation, or elution, of Ca from the columns. The relative concentrations greater than 1 indicate Ca, and to a lesser extent Fe and Mn, are eluting from the columns at much higher concentrations than the influent leachate at various pore fractions. The area under the Ca curves in figure 3 increases in proportion to the percentage of clay in the column.

To quantify the observed attenuation, the area under each curve was integrated between pore fractions 1 and 11. The area between 0 and 1 pore fraction was not included because it merely indicated the displacement of the deionized water initially present in the column. The total area was that bounded by 10 pore volumes and relative concentrations between 0 and 1. The relative attenuation number (ATN) was obtained by subtracting the area under the curve from the total area and was expressed as a percentage. The ATN numbers are unique for each element and each clay and express the relative mobilities of each element through each particular clay or clay-mixture column.

The attenuation number was computed for all columns and each chemical constituent studied. The mean attenuation number for each chemical constituent was used to rank the constituents according to their relative mobility through the clay columns (table 4). In the Du Page leachate, Al, Cu, Ni, Cr, As, SO_4, and PO_4 were found in such low concentrations that no attenuation order could be determined. The results showed that greater amounts of the metals Pb, Zn, Cd, and Hg than any other element were removed from leachate, averaging about 97 percent attenuation for 10 pore volumes leached. The data for 2 percent montmorillonite (fig. 2A) show that Cd and Hg were the most mobile of the metals studied. Measurable amounts of Cd and Hg appeared in the effluents of the 2 percent clay column after about 6 pore volumes were leached. Only traces of Cd and Hg appeared in the effluents of the 8 percent and 16 percent clay treatments (figs. 2B, 2C).

TABLE 4—RANK OF CHEMICAL CONSTITUENTS IN MUNICIPAL LEACHATE ACCORDING TO RELATIVE MOBILITY THROUGH CLAY MINERAL COLUMNS

Chemical constituent	Mean attenuation number	Qualitative grouping
Pb	99.8	High
Zn	97.2	
Cd	97.0	
Hg	96.8	
Fe	58.4	Moderate
Si	54.7	
K	38.2	
NH_4	37.1	
Mg	29.3	
COD	21.3	Low
Na	15.4	
Cl	10.7	
B	-11.8	Negative (elution)
Mn	-95.4	
Ca	-656.7	

Removals of Pb and Zn were very high in all columns. Results obtained from chemical analysis of sectioned columns revealed large accumulations of all four metals in the surface 2 to 4 cm of each column, including the 100 percent sand column.

Moderate attenuation was observed for the leachate constituents Fe, Si, K, NH_4, and Mg, which had attenuation values ranging between 58.4 percent and 29.3 percent. Little attenuation was found for COD, Na, and Cl, attenuation percentages for which ranged between 21.3 and 10.7. The elements Ca, Mn, and B not only were unattenuated by the clays, but were found in substantially higher concentrations in the column effluents than in the influent leachate.

Mechanisms of Attenuation

To determine what mechanisms were responsible for the observed differences in attenuation for each leachate constituent, the effect of clay type was investigated. The mean attenuation numbers of chemical constituents obtained for each clay appear in table 5. They show that no significant difference in attenuation by the three clay minerals was observed for the metals (Pb, Cd, Hg, Fe, and Zn), for B, or for Cl. Illite and kaolinite attenuated Si significantly better than montmorillonite. Kaolinite was found to elute Mn in significantly higher amounts than either montmorillonite or illite. No significant difference in COD attenuation between montmorillonite and illite was found, and both attenuated COD significantly better than kaolinite. Montmorillonite was found to attenuate the cations Na, K, NH_4, and Mg and to elute Ca to a significantly greater degree than illite and kaolinite.

TABLE 5—ATTENUATION OF CHEMICAL CONSTITUENTS IN MUNICIPAL LEACHATES BY THREE CLAY MINERALS

Chemical constituent	Attenuation number (ATN) Montmorillonite	Illite	Kaolinite
Pb	99.6*	100.0	99.9
Zn	97.7	98.6	98.1
Cd	96.7	100.0	97.5
Hg	98.4	98.1	95.2
Fe	34.8	82.8	67.6
Si	39.2	81.6	71.2
K	58.9	31.0	23.2
NH_4	54.8	31.0	25.1
Mg	48.2	19.7	18.1
COD	24.6	23.2	16.2
Na	20.6	16.4	9.7
Cl	9.3	13.5	14.3
B	-16.1†	-12.8	-11.5
Mn	-73.2	-6.4	-266.2
Ca	-885.5	-233.2	-190.2

* Underlining indicates no significant difference (0.05).

† Minus numbers indicate elution.

Removal of Pb, Zn, Cd, and Hg could be attributed to cation exchange replaceability, but a precipitation mechanism appears a more plausible cause. Precipitation could involve formation of metal hydroxides or carbonates, brought about by the relatively high pH and high bicarbonate ion concentration found in the leachate (table 2). The precipitation mechanism is given further credence by the measurements of the effluent concentrations in sand columns, which have no cation exchange capacity. No Pb and markedly reduced concentrations of Zn, Cd, and Hg eluted from the sand columns. Our equilibrium studies of the effect of pH on removal of metal ions by clay also support a precipitation mechanism.

That the four metals are attenuated by precipitation is consistent with the fact that no differences in attenuation means were found among the three clays. Because these four metals exist in solution as cations, a significant effect of clay type would be expected if cation exchange were the attenuation mechanism. That no such effect was observed was taken as additional evidence that the primary attenuation mechanism for these four metal ions is precipitation.

To determine whether the greater attenuation of the cations Na, K, NH_4, and Mg and the elution of Ca by montmorillonite were caused by its higher cation exchange capacity, the attenuation numbers were plotted as a function of the cation exchange capacity (CEC) of the three clay minerals in figures 4 and 5. The very highly significant linear regression of attenuation numbers as a function of CEC led to the conclusion that the principal attenuation mechanism for Na, K, NH_4, and Mg was the cation exchange of these constituents for Ca. Ca was the predominant exchangeable cation present on the clays when leaching began (table 1). To further confirm that this mechanism was responsible, a mass balance for these five cations was computed for data presented in figure 2. The sums of the amounts of Na, K, NH_4, and Mg removed from the leachate agreed within 3 percent with the amount of Ca eluted. Increases in the concentration of alkaline earth metals in ground water preceding a leachate plume have been observed in the field during monitoring of ground-water chemistry around landfill sites. Such an increase was postulated to be the result of the same mechanism that caused the Ca elution from the columns in this study. It has been termed the "hardness halo," and will be discussed further in the section on field verification.

No significant linear regression of attenuation as a function of either CEC or clay percentage was obtained for Fe, Si, COD, Cl, B, or Mn, ex-

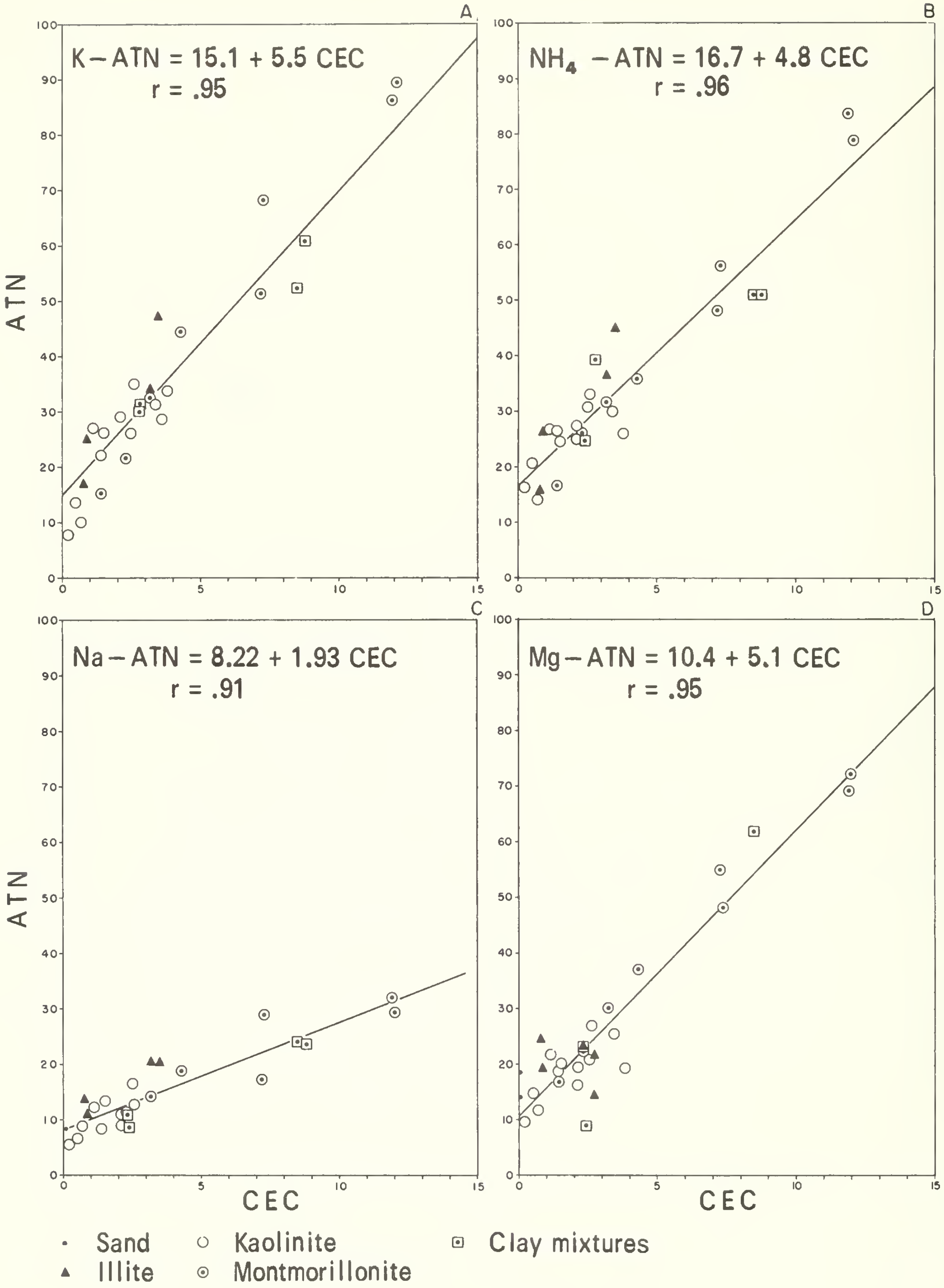

Fig. 4 - The attenuation number related to cation exchange capacity (A) K, (B) NH_4, (C) Na, and (D) Mg.

cept for a very highly significant one obtained for Mn elution and clay percentage. The results of the regression of Mn elution as the percentage of kaolinite and montmorillonite increased are presented in figure 5B. No sig-

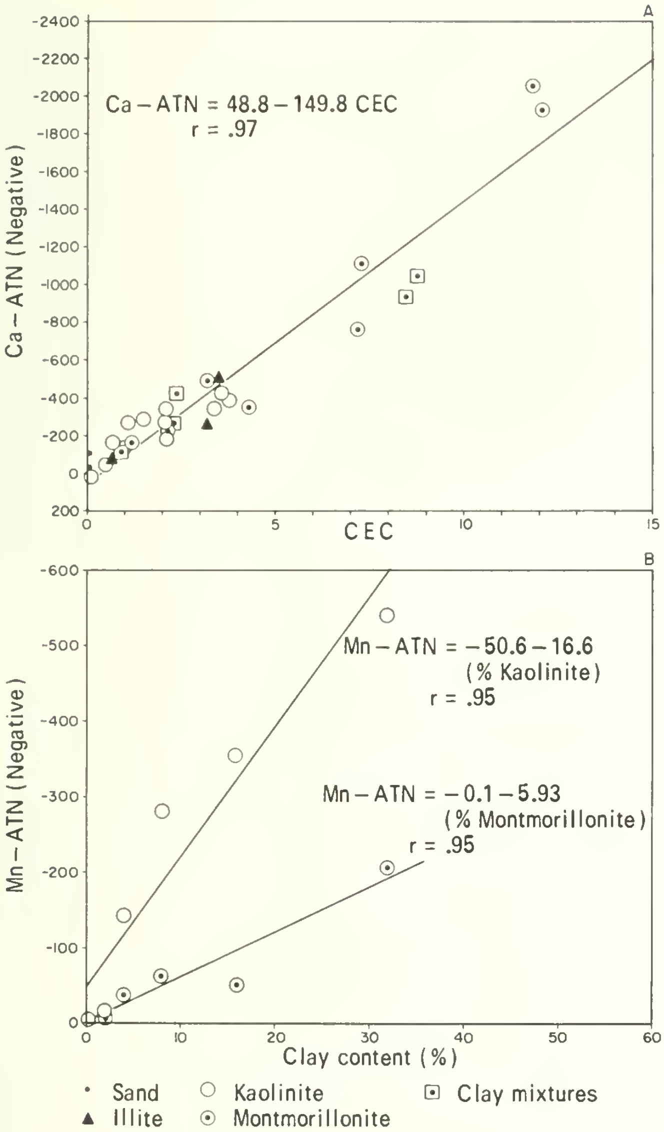

Fig. 5 - (A) Ca attenuation number related to cation exchange capacity.
(B) Mn attenuation number related to clay percentage.

nificant linear regression could be obtained with illitic clay because only two illite columns were used. The data in the figure (5B) show that approximately three times as much Mn eluted from the kaolinite-containing columns as from the montmorillonite columns. Table 1 indicates that kaolinite contains only slightly more total Mn than montmorillonite does. However, surface Mn is three times more abundant on kaolinite than on montmorillonite, an abundance that corresponds to the increased elution from the kaolinite columns. No correlation of Mn elution was observed with CEC, and the amounts of surface-extractable Mn correlate with the amounts eluted from the various columns. These facts, along with the anaerobic conditions in the columns, led to the conclusion that Mn elution is due to the reduction of surface coatings of Mn compounds on the clays to more soluble reduced ionic species. The increase in Mn elution from kaolinite columns is proportional to, and apparently due to, the larger amount of Mn on the surface, where it is readily available for reduction and solubilization by the anaerobic leachate.

The behavior of Fe is similar to that of Mn; however, Fe is more sensitive to the oxidation potential in the leachate than Mn. During the early stages of leaching, Fe also was solubilized and eluted from the columns (fig. 3). However, unlike Mn, Fe showed a net attenuation of 58.4 percent for the entire 10 pore volumes leached. The results of this study, therefore, indicate that Fe may be either eluted or not attenuated by clay liners if the leachate is strongly anaerobic, or it may be strongly attenuated under weakly anaerobic conditions.

Other data from this study indicate that attenuation of COD was relatively low after Du Page leachate had passed through the clay columns. This result agrees with those of Urioste (1971), who reported poor removal of COD when leachate was ponded on soils. The lack of a strong clay effect and of a significant correlation of attenuation of COD with either clay percentage or CEC indicates that the observed attenuation was probably the result of microbial degradation of the organic compounds. The fact that the leachate is relatively old probably accounts for the relatively low reduction in COD. It has only a small percentage of readily degradable organic material and a low nutrient status, owing to the lack of PO_4 (table 2).

Chloride attenuation was also relatively low, only 10.7 percent. This low attenuation is not surprising, because Cl is considered as a mobile, noninteracting anion in soil systems. The low Cl attenuation was not a function of the type or amount of clay mineral present but is attributed to physical dispersion in the porous column media (with perhaps a small amount of interaction at anion exchange sites on the clay) or to other chemical reactions.

Since Cl is a negative ion, it would be attracted only by the positive charge at the edge of the clay minerals. Oxygen and OH are the negative ions of the lattice, and any other negative ion would have to be nearly the same size as the oxygen ion in order to coordinate with and continue or substitute for the oxygen. As the chloride ion has about 2½ times the volume of the oxygen ion, it is too large to replace or coordinate with the oxygen and hydroxyl ions, although fluorine can do so because it is about the same size as the oxygen and hydroxyl ions.

No attenuation of boron was observed in this study; rather, a small elution of boron from the columns took place throughout the leaching experiment. This may be interpreted as a slight solubilization of B from the clay minerals or sand in the columns. However, no effect of type or percentage of clay and no changes in elution with leaching time were found during the study. These facts have led to the conclusion that the B results may be an artifact of the experiment. It has been suggested that B may be dissolving from the borosilicate glass tubing used throughout the apparatus. More likely, B may be solubilized from the spun glass wool used as a filter to keep sand and clay from migrating into the five manometers and the outflow tubing (fig. 1). The high surface area of the spun glass and the neutral pH of the leachate make it plausible that the boron elution may be due to contamination. In any case, no attenuation of boron was observed in this study.

Attenuation Properties of Clay Minerals

The results presented in figure 4 and table 5 permit the three clay minerals to be ranked, according to their over-all attenuating ability for the chemical constituents found in municipal leachate, as follows:

montmorillonite > illite > kaolinite.

The montmorillonite used in this study has properties similar to those of smectites produced by weathering of micas, chlorites, and other crystalline minerals. The cation exchange capacity is lower than that for montmorillonite produced from weathering of volcanic ash and basaltic rocks.

The montmorillonite used forms rocks (e.g., Porter's Creek Clay) that have much higher hydraulic conductivities than the Wyoming type of montmorillonite. Such high hydraulic conductivity should make this montmorillonite more useful for landfill liners in humid climates than some other types of montmorillonite. With its high cation exchange capacity, it would adsorb more of the cations in the leachate than either illite or kaolinite. Its greater hydraulic conductivity, compared with that of many other types of montmorillonite, would allow more water to pass through a liner and would lessen the hazard of lateral seepage from the sides of the landfill in humid climates.

Some sodium montmorillonites tend to shrink when sodium is exchanged for divalent and trivalent cations or when salt concentrations are high. This shrinkage sets up tension, which in turn produces cracks called syneresis cracks. Syneresis cracks were common in irrigation ditches in Colorado that were lined with sodium montmorillonite (R. D. Dirmeyer, Jr., personal communication, 1961). Shrinkage could be reduced considerably by using calcium montmorillonites and mixing them with other earth materials (*e.g.*, 16 to 32 percent montmorillonite and 68 to 84 percent sand).

The kaolinite used in this study is a fine-grained rock in which the crystallinity of the kaolinite is poor. It has a high cation exchange capacity compared with that of other kaolinites. Well crystallized kaolinites with large crystals have a cation exchange capacity of 1 to 5 meq/100 g. The kaolinite used in this study would be better suited for landfill liners than most kaolinites, for its hydraulic conductivity is lower than that of well crystallized kaolinite with large crystals. The kaolinite in most sediments has a cation exchange capacity and hydraulic conductivity between those of the kaolinite used and the well crystallized kaolinites.

The illite used is similar in cation exchange capacity and hydraulic conductivity to the illite found in most sediments. The sediment from which the experimental illite was taken contained only the one clay mineral, whereas most sediments that contain illite also contain other clay minerals.

It was concluded that the attenuation order was due principally to the cation exchange capacities of the three clays.

POLLUTION HAZARD OF LEACHATE

In addition to determining the relative mobilities of the various chemical constituents of leachate through clays (liner materials), their relative pollution hazard should be evaluated. Ranking wastes in terms of their existing or potential threats to public health and/or the environment has been the subject of the Priority Ranking System suggested for development by the U.S. EPA (1973a).

The priority ranking formula is:

$$R = Q/CP \qquad [1]$$

where R = ranking factor,
Q = annual production quantity for the waste being ranked, and
CP = critical product for the waste being ranked.

A critical product is the lowest concentration at which any hazard becomes manifest in a given environment, multiplied by an index representative of the waste's mobility into that environment. Thus, for a municipal leachate that would be discharged through a clay liner or soil into an aquifer used for drinking water, the toxicity factor could be the public water supply limits for the given element, and the mobility index could be the attenuation numbers derived above.

Evaluation of the critical product for municipal leachates moving through soils or clay liners proved to be awkward and unsatisfactory for several reasons. The first problem encountered was that negative attenuation numbers, such as those obtained for calcium, were not accommodated by the formula. A transformation of the data would be necessary to express the negative numbers in a manner that could be used in the CP formulation.

The second problem encountered was evaluation of the CP for the four metals. An upper boundary on the attenuation number, such as the 100 percent removal, used to express the metal ions removed from leachate is not allowed conceptually by the formula. Instead, what is required is the actual attenuation determined by leaching until breakthrough of the particular element is achieved. For Pb, an estimated 300 pore volumes would have to be leached through an average column to achieve breakthrough. It was deemed impractical to actually measure the breakthrough of the metals, and estimating their breakthrough required additional analytical data that could cause errors in estimating the pollution hazard.

A third problem with the evaluation of the pollution hazard by using the CP was that it was not specific for the waste being evaluated in that the concentration of an element in the waste did not enter into the evaluation of the hazard. That this is a serious fault can be illustrated by simple examples: an element with a relatively high toxicity and mobility index could get a high hazard rating, even though only a trace was present in the waste; conversely, an element with a relatively low toxicity and mobility could receive a low hazard rating even though it was present in very high concentrations.

A fourth criticism of the CP rating was that it was conceptually illogical because large CP values indicated a low pollution hazard and, conversely, a very small number represented a very high hazard. We considered it more logical to express high pollution hazards as large numbers when a relative scale was used or when pollution potentials were evaluated.

To overcome these objections to the CP formulation of a pollution hazard index for municipal leachates, we changed the ranking equation to read as follows:

$$R = (Q)\,(HI) \qquad [2]$$

where R and Q are as previously defined and HI is the pollution hazard index for the waste. The pollution hazard index (HI) is a toxicity index for the element within a given leachate, multiplied by a mobility index for the element in a particular leachate-clay system. The pollution hazard for the whole leachate is that for the constituent with the highest hazard within the particular leachate.

$$HI = \left(\frac{C}{DWS}\right)(100 - ATN) \qquad [3]$$

where C = the effective concentration of the chemical constituent,
DWS = the drinking water standard (U.S. EPA, 1973b), and
ATN = the attenuation number for the given element.

The effective concentration is defined as the concentration of the chemical constituent in the leachate plus the concentration of the constituent that may be leached from the soil or clay. When attenuation is occurring, the effective concentration is merely the concentration of the constituent in the influent leachate. When elution from the columns is occurring, as it did for the three elements B, Ca, and Mn, the effective concentration is the leachate concentration plus the concentration eluted from the column. Table 6 presents the 15 chemical constituents for which ATN values are available, ranked according to their pollution hazard as determined by equation 3.

TABLE 6—CHEMICAL CONSTITUENTS IN DU PAGE LEACHATE RANKED ACCORDING TO POLLUTION HAZARD

Chemical constituent	Effective concentration / Drinking water standard	Toxicity index	Mobility index	Hazard index
NH_4	862/0.5	1724.	62.9	108,440.
B	(29.9 + 3.5)/1.0	33.4	111.8	3,734.
COD	1340/50	26.8	78.7	2,109.
Hg	0.87/0.002	435.	3.2	1,392.
Cl	3484/250	13.9	89.3	1,241.
Ca	(46.8 + 307.3)/250*	1.42	756.7	1,072.
Cd	1.95/0.01	195.	3.0	585.
Fe	4.2/0.3	14.0	41.6	582.
Na	748/270	2.77	84.6	234.
Mn	(0.02 + 0.02)/0.05	0.78	195.4	153.
K	501/250*	2.00	61.8	123.
Mg	233/250*	0.93	70.7	65.7
Pb	4.46/0.05	89.2	0.2	17.8
Zn	18.8/5.0	3.76	2.8	10.5
Si	14.9/250*	0.06	45.3	2.7

* Actual value not established by EPA; therefore assumed to be the same as chloride.

The results in table 6 give a reasonable ranking of the chemical constituents in terms of what would be expected from a gross overview of the data. The ranking system has the advantage of quantifying the expected pollution hazard of a given leachate and allows comparisons of the pollution hazards of one leachate with another. The ranking system also focuses attention on the chemical constituent with the highest pollution potential. In Du Page leachate, NH_4 was found to have the highest pollution hazard. In a fresh leachate, COD might be expected to have the highest pollution potential. However, in the Du Page leachate the hazard index clearly indicates that NH_4 is a pollution hazard about 30 times greater than any other constituent found in that particular leachate.

We feel that the proposed system of ranking pollution hazards in municipal leachates (equation 3) overcomes the objections posed previously for the CP component of the Priority Ranking System. The toxicity index can in most cases be readily computed from a chemical analysis of the leachate.

The evaluation of the toxicity index is flexible in that drinking water standards need not be the criteria. LD_{50} (lethal dose for 50 percent of the population) values, or some other toxicity evaluation, can be used in place of drinking water standards. What we think is important is the computation of the ratio of the actual waste concentration relative to whichever toxicity evaluator is used. The mobility index, however, must be determined experimentally or estimated from the data presented in this paper. The results of this study indicate that the mobility index will be a function of the CEC of the earth material, the cations initially present on the exchange complex, the chemical composition of the leachate, and the pH of the leachate.

HARDNESS HALO

Figure 3 illustrates the negative attenuation or elution of Ca, Fe, and Mn from the columns containing 2, 8, and 16 percent montmorillonite clay in sand. The relative concentrations greater than 1 indicate Ca and, to a lesser extent, Fe and Mn are eluting from the column at a much higher concentration than is present in the influent leachate at various pore fractions. The area under the Ca curves increased in proportion to the percentage of clay in the column and was quantified by integration between pore fractions 1 and 11 and assigned a relative attenuation number (ATN) (table 4).

The elution of Ca from the columns was attributed to an ion-exchange mechanism: the replacement of the Ca bonded to the clays at their cation exchange positions by other ions in the leachate.

Soils in much of Illinois are rich in carbonates, Ca is generally dominant in the cation exchange positions of the clays, and free carbonates are present in all parts of the soils except the leached zone. The presence of excessive hardness in the vicinity of sources of pollution has been reported in a number of articles, but its origin has rarely been discussed. In a Du Page County study (Zeizel et al., 1962), hardness, as $CaCO_3$, in the shallow carbonate aquifer in two areas of the county exceeded 1000 parts per million (ppm) (fig. 6). The eastern area is a fairly heavily developed residential area where the glacial drift, which protects the aquifer from pollution, is relatively thin. Although no specific source for the high hardness has been found, it is most likely due to the high concentration of home septic systems, which release an effluent similar in composition to landfill leachate. The western area of high hardness, near West Chicago, is thought to have resulted from the discharge of large volumes of chemical waste to surface ponds.

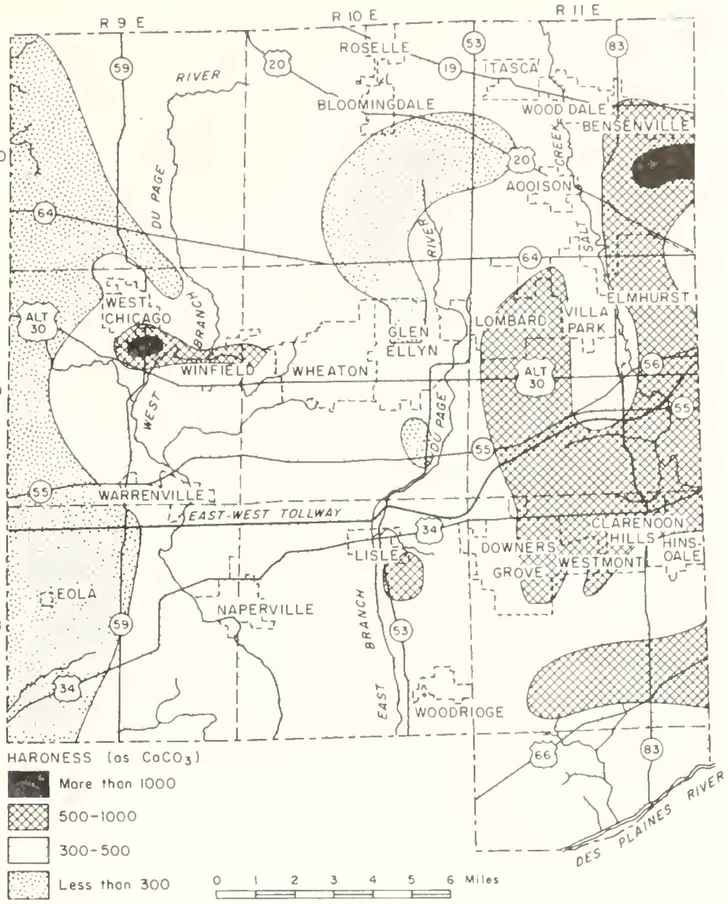

Fig. 6 - Hardness of water expressed as $CaCO_3$, in the Silurian Dolomite aquifer in Du Page County, northeastern Illinois (from Zeizel et al., 1962).

Other examples can be found in Anderson and Dornbush's (1967) study of a sanitary landfill in South Dakota, and Walker's (1969) discussion of ground-water pollution in Illinois. Most recently, Henning et al. (1975) found a high calcium content in monitoring wells very close to a landfill trench at Mentor, Ohio; the calcium concentrations decreased with distance from the fill and in the refuse were lower than in the closest wells.

Hughes, Landon, and Farvolden (1971) published the results of studies of five landfills in northeastern Illinois, including the old Du Page County landfill from which the leachate was taken for this study. Monitoring continued for 3 years following the completion of that report. Figure 7 was based on data from the Winnetka and old Du Page landfills.

The Winnetka data (fig. 7) show considerable scatter. This may be partly due to a mixture of sampling points, some in the fine-grained alluvium and some in the glacial till, that have somewhat different properties. However, these data suggest that the hardness approaches background within 9 to 15 meters of the refuse, which is somewhat less than the limit that the chloride ion traveled (Hughes, Landon, and Farvolden, 1971). The chloride ion is probably the best indicator of pollution in the particular environment of the landfills. The four data points from piezometer nest LW3 follow this pattern.

The till under the old Du Page landfill clearly illustrates the increase and subsequent decrease in hardness. The till is separated from the

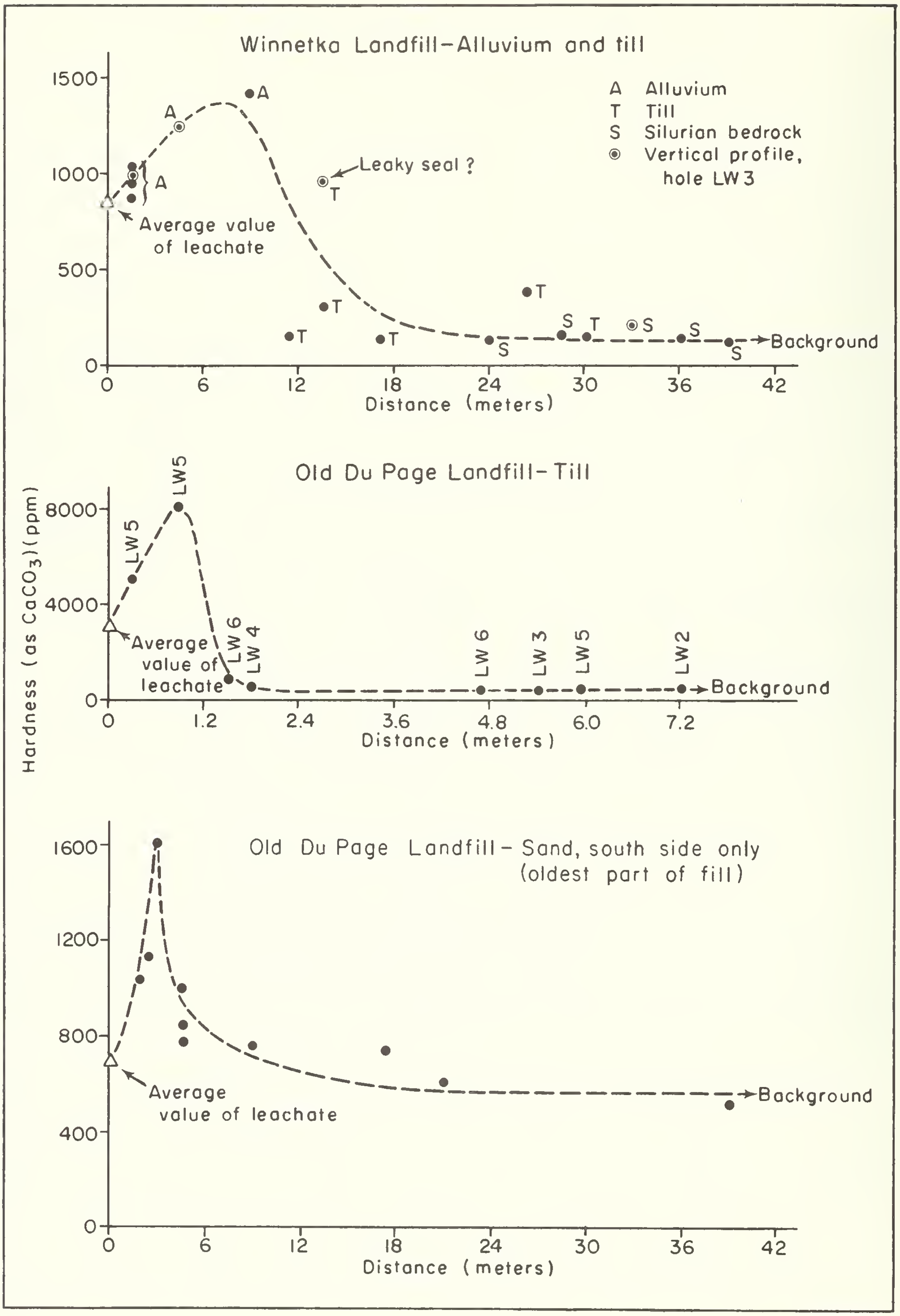

Fig. 7 - "Hardness halo" effect shown as a function of distance (m) from the Winnetka and Du Page landfills in northeastern Illinois.

refuse by 1 to 1.5 meters of sand. The hardness returns to background within about 1.5 meters of travel, about half of the estimated distance the chloride ion travels (Hughes, Landon, and Farvolden, 1971). Note in particular the values shown for piezometer nests LW5 and LW6. These data points are all for the younger, north part of the fill; data from the older parts of the fill do not fit the same curve (all hardness concentrations are too low).

The surficial sand transmits leachate-contaminated water southward from the older parts of the Du Page landfill, and the water shows a similar hardness distribution. The hardness levels are much lower in the old refuse in this area, and all the values reflect that lower concentration. The hardness returns to background levels within 9 to 15 meters. However, the chloride ion moved 240 to 300 meters in the permeable sand layer.

All these data clearly show the presence of the "hardness halo" that results from the movement of leachate into the surrounding till and sands. They also show that the rate of advance of the hardness front is less than that of the chloride ion. The distance traveled varied from slightly less to approximately 10 percent of that of the chloride ion; this probably is controlled by the nature of the materials, cation exchange reactions, concentrations in the leachate, and ground-water flow rates. Nevertheless, all the data show the hardness of the water in the sediments is greater than that in the leachate.

HYDRAULIC CONDUCTIVITY

The results of initial hydraulic conductivity and bulk density measurements of the column contents in table 3 indicate a wide range of hydraulic conductivities that agree with those expected under field conditions from similar materials (Todd, 1959). The relatively high bulk densities and slow flow rates used in the laboratory closely simulate the conditions observed in the field, making it possible to extrapolate the results and conclusions of the laboratory studies to those obtained in the field.

During the initial stage of the experiment, the columns were leached with deionized water until steady-state conditions were reached. The columns containing low percentages of clay reached hydraulic equilibrium relatively rapidly, while the columns with high percentages of clay required leaching for well over a month to achieve steady manometer readings. When hydraulic equilibrium was reached, as indicated by steady flow rates and relatively constant manometer readings from the five manometers placed along the entire length of each column, the leachate was added to the column.

Significant reductions in hydraulic conductivity and significant differences in the reductions between natural and sterile leachate were observed. The changes in hydraulic conductivity that occurred in the kaolinite columns during the experiment were reported by Griffin and Shimp (1975). The results of changes in hydraulic conductivity observed in columns containing montmorillonite, kaolinite, and illite clays are shown in figures 8, 9, and 10. The data presented in these figures were statistically smoothed by using the five-member moving-average method to clarify the trends in the data. The

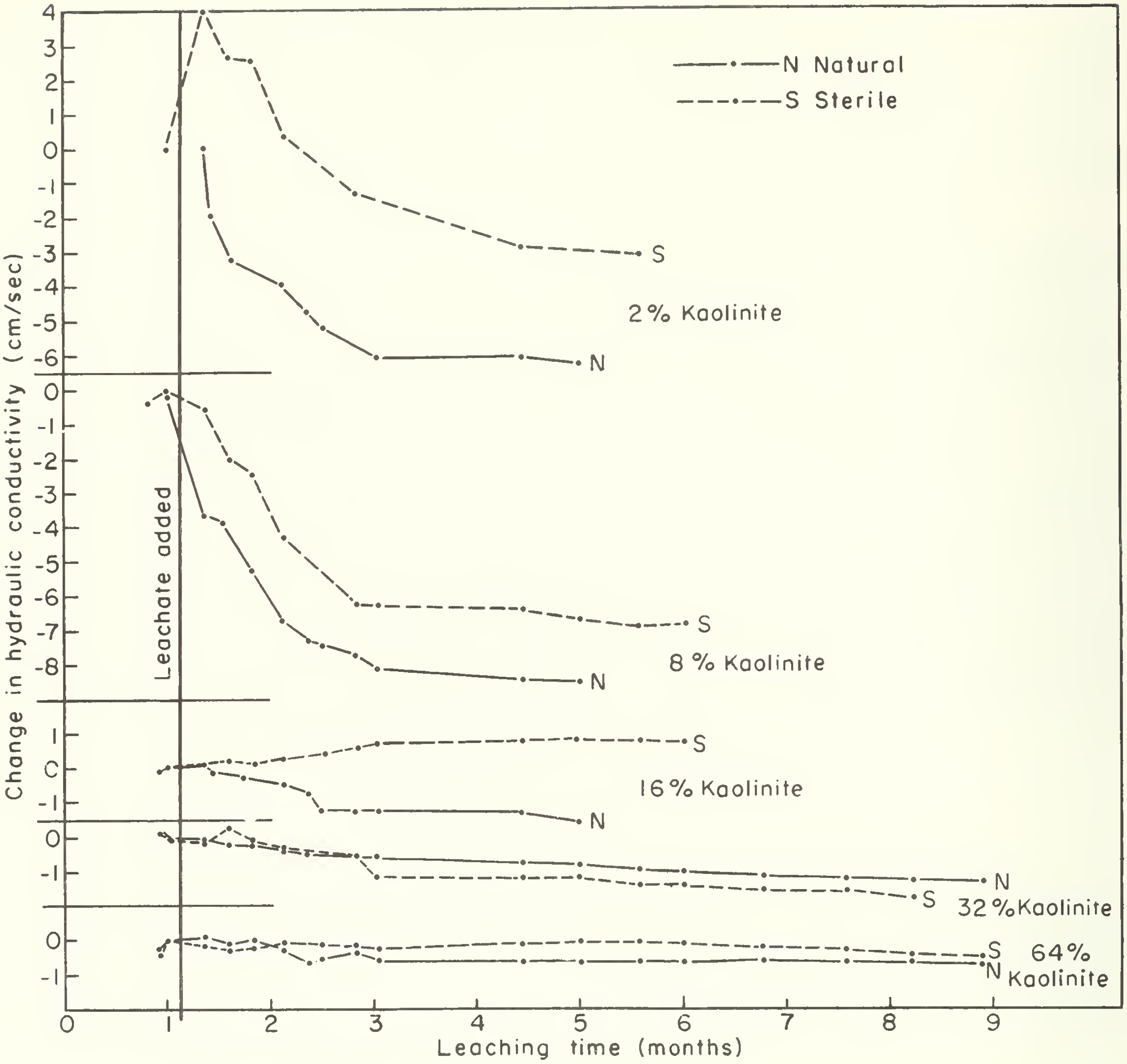

Fig. 8 - Hydraulic conductivity of kaolinite-sand columns as a function of leaching time.

data were analyzed statistically to determine whether any significant differences occurred in the hydraulic conductivity of sterile leachate and that of natural leachate. The data from the columns containing 4 percent kaolinite were rejected from the analysis when they were found to deviate by more than three standard deviations from the over-all mean change in hydraulic conductivity observed for all other columns. The manometer readings indicated that the outflow tubes were plugged. Why only the columns containing 4 percent kaolinite had this problem is not clear.

The statistical analysis indicated that columns leached with natural leachate had significantly (0.05 level) greater reductions in hydraulic conductivity than those leached with sterile leachate (figs. 8, 9, and 10). Furthermore, the statistical analysis showed that columns containing montmorillonite had significantly larger average reductions in permeability than did

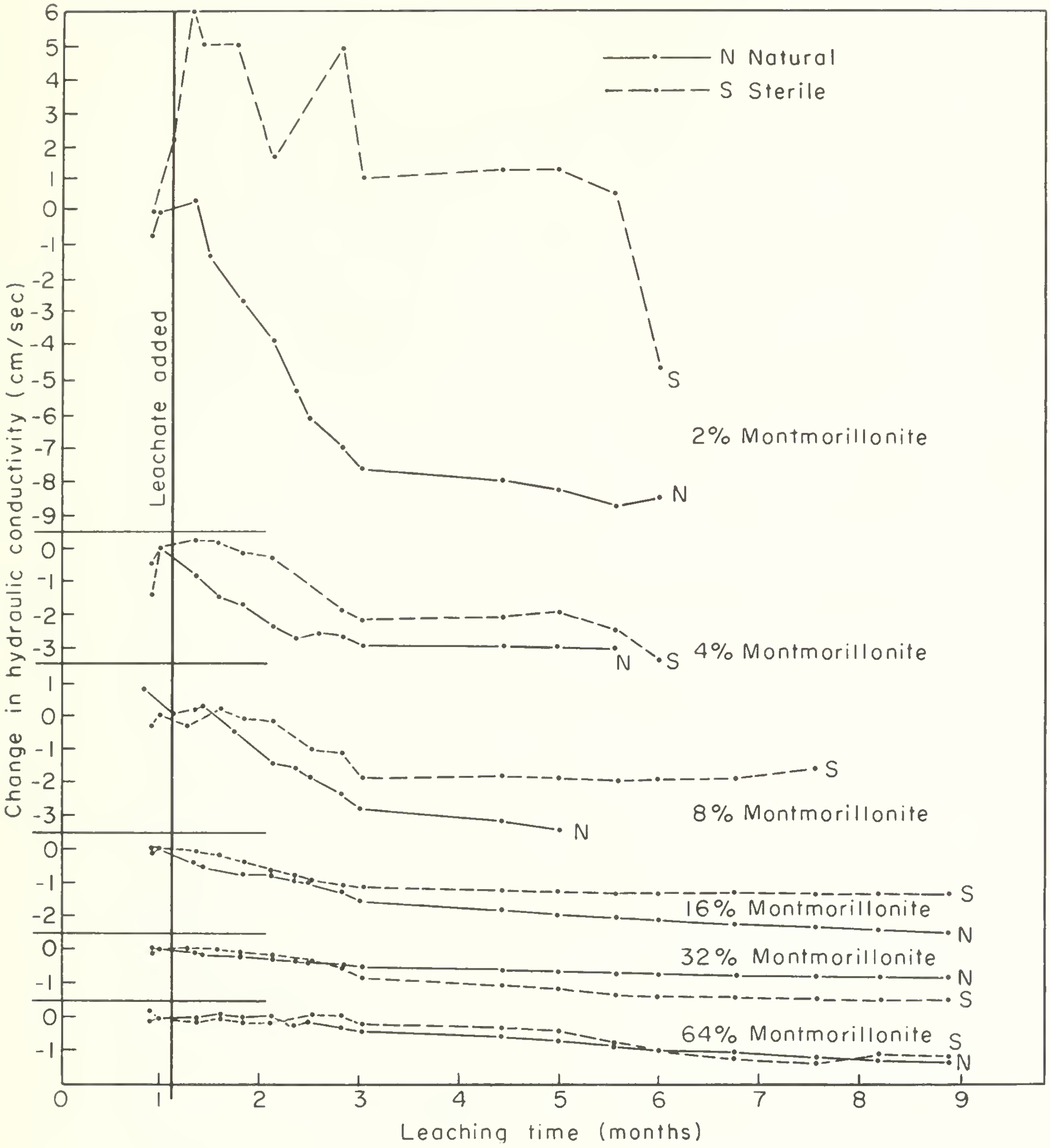

Fig. 9 - Hydraulic conductivity of montmorillonite-sand columns as a function of leaching time.

those containing kaolinite or illite and that there was no significant difference between the kaolinite and illite columns. Montmorillonite's tendency to swell when wet explains its reduced permeability.

Field data to support these observations are not so clear-cut as the supportive data for the "hardness halo." Fewer field tests have been made for hydraulic conductivity than chemical tests for water quality. In addition, field tests for hydraulic conductivity may be accurate to only approximately half an order of magnitude.

At the Winnetka landfill, 23 hydraulic conductivity tests were made, seven on refuse, four on alluvium, and seven on till. The resultant data are

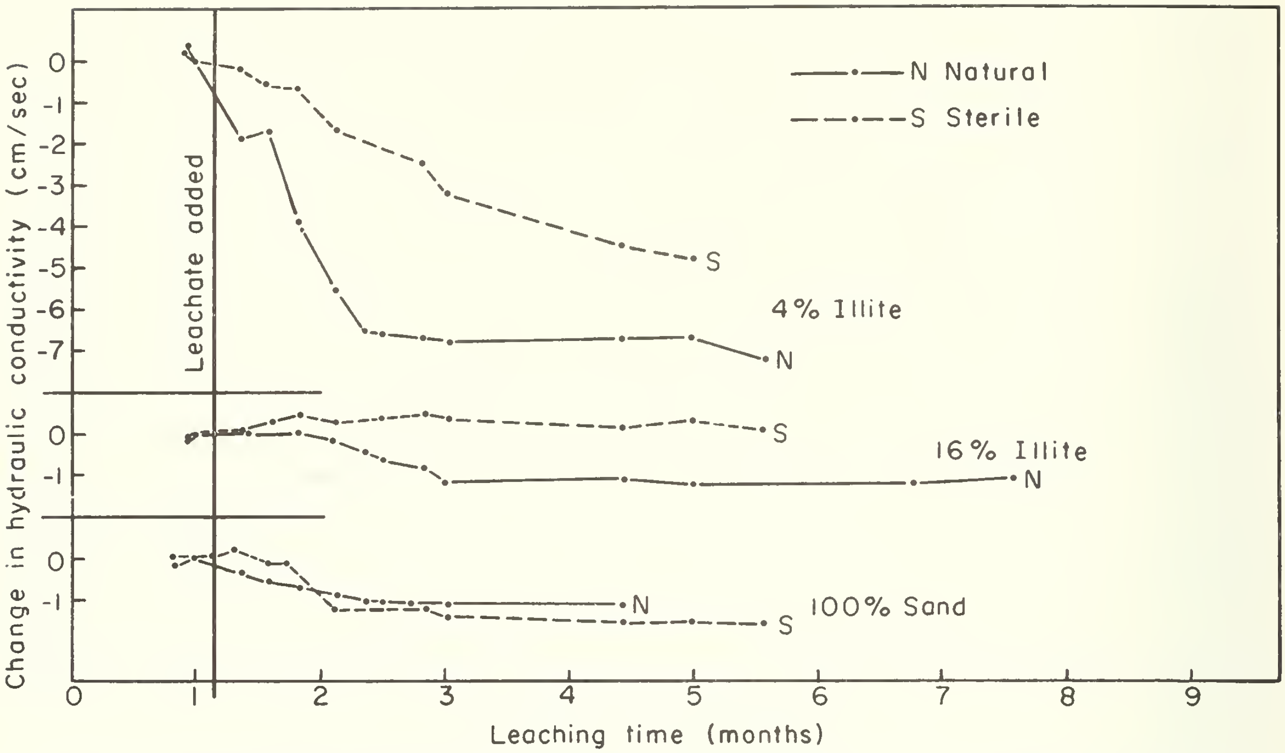

Fig. 10 - Hydraulic conductivity of illite-sand columns as a function of leaching time.

too scattered to show any significant differences with distance from the refuse.

At the old Du Page County landfill, 34 field tests were made for hydraulic conductivity—14 on refuse, 14 on sand, and six on till. The data on the hydraulic conductivity of the sand, all made south of the fill, suggest some reduction in hydraulic conductivity. Ten of the tests made on monitoring wells less than 6 meters from the fill showed a mean hydraulic conductivity of 4.32×10^{-4} cm/sec (range 1.9×10^{-3} to 1.9×10^{-7}). Four tests on monitoring wells more than 12 meters from the refuse showed a mean conductivity of 2.59×10^{-3} cm/sec (range 7.6×10^{-3} to 9.5×10^{-4}). The data are not statistically significant, but they do seem to indicate a possible reduction in hydraulic conductivity similar to that noted in the laboratory.

The reductions in hydraulic conductivity observed in this experiment with the Du Page leachate seem particularly significant. The Du Page leachate is approximately 15 years old (Hughes, Landon, and Farvolden, 1971) and contains a relatively low percentage of organic compounds that are readily degradable by microorganisms (table 2). In addition, this leachate has a low nutrient status, both phosphate and sulfate in detectable quantities being absent. Much higher amounts of microbial growth and plugging might be expected from a younger leachate.

These results have led to the conclusion that if clay liners, natural or man-made, that are similar in composition to those studied are used in municipal landfills, significant reductions in hydraulic conductivity can be expected because of microbial growth. Slightly higher reductions in hydraulic conductivity can be expected from montmorillonite clays, apparently owing to their tendency to swell.

ATTENUATION OF LEACHATE

From collection of the leachate through the establishment of hydraulic equilibrium, the leachate was refrigerated (3° to 5° C), with either argon or a sterilizing gas introduced slowly over the top of the leachate in each drum. Weekly chemical analyses of the leachate made to monitor possible changes in composition revealed that the COD of the sterile drum was steadily rising. It was determined that the active component of the sterilant, ethylene oxide, was able to react with the chloride ion present in the leachate. The chloride acted as a nucleophile to produce ethylene chlorohydrin (Rosenkranz and Wibdkowski, 1974). When it was discovered that the COD was rising rapidly, the use of the sterilizing gas was discontinued. Argon was then used as the purging gas for both drums, and mercuric nitrate salt was added to the sterile drum to maintain its sterility. Further monitoring of both drums was continued at approximately 1-week intervals during the 10 months the columns were leached. The COD values remained constant at the value recorded when the use of sterilizing gas was discontinued. The value for COD and other constituents reported in table 2 is the average of the 37 separate analyses performed during the 10 months of leaching.

Determination of the attenuation of chloride and the other major components of Du Page leachate was described above. The results indicated that in the columns leached with sterile leachate an average of 6 percent more chloride was attenuated than in columns leached with the natural leachate. This greater attenuation is attributed to the reaction of chloride with the ethylene oxide to form ethylene chlorohydrin. Other than the slight increase in chloride attenuation, apparently no significant difference was caused by the increase in COD in the sterile leachate compared to the natural leachate.

There were, however, other significant differences between the sterile and natural leachate treatments that were not attributed to the higher COD of the sterile leachate. The difference observed in Mn elution from the columns is shown in figure 11. A negative attenuation number indicates that more Mn eluted from the column than was present in the influent leachate. Much higher levels of Mn were found in effluents from the columns leached with natural leachate. As previously stated, this elution was due to reduction of surface coatings of Mn oxides on the clays by the anaerobic leachates, a conclusion that is further verified by the difference in Mn elution between the natural and sterile leachate treatments. The difference is attributed to the stronger anaerobic environment provided by the active microorganisms present in natural leachate.

Table 2 shows that the average Eh (oxidation potential) reading of the natural leachate was 10 times lower than that of the sterile leachate, even though both were well within the anaerobic range (Eh readings less than 197 mv are considered to reflect anaerobic conditions). A similar result was obtained for Fe in that significantly (0.05 level) greater mobility of Fe was found in columns leached with natural leachate than in those leached with sterile leachate. A mechanism similar to that for Mn is postulated as the reason for the observed differences in Fe mobility between the natural and sterile leachates.

No significant difference in attenuation between the normal and sterile leachates was found for Ca, Mg, Na, K, NH_4, Pb, Hg, Zn, and Cd.

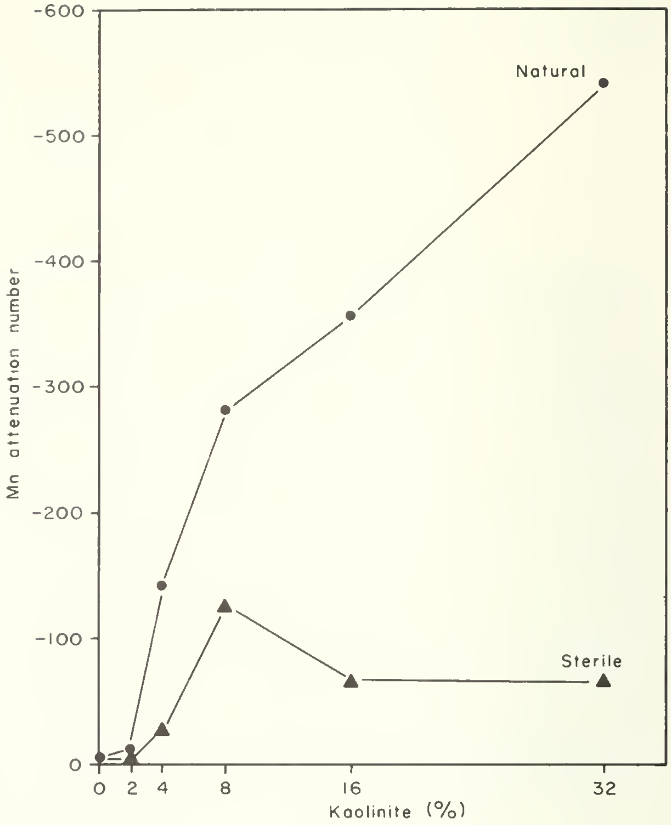

Fig. 11 - Manganese elution related to percentage of kaolinite leached with natural and sterile leachate.

LANDFILL DESIGN

General Considerations

The design of a landfill should take into account three factors: the hydrologic system governing direction of pollutant travel, the geochemistry of the water-sediment system, and the release rate of unattenuated pollutants to surface or ground waters. The first has been the subject of several papers and will not be discussed here.

Current landfill design and engineering practice call for the construction of clay liners, either natural or artificial, that are extremely thick and contain high percentages of clay. The intention is to create relatively impermeable liners that will keep the leachate in and therefore protect the ground-water resources. This approach creates difficulties in humid climates where infiltration exceeds the capacity of the liner to dissipate the leachate, causing what is referred to as the "bathtub" effect, wherein the relatively impermeable clay liner acts as a bathtub, filling up with leachate and then overflowing. The overflow takes the form of leachate springs on the surface and results in surface water pollution and environmental degradation rather than ground-water pollution. Neither form of pollution is either desirable or necessary if the sanitary landfill is properly designed and constructed.

Optimal Attenuation and Hydraulic Conductivity

The results of our chemical attenuation study indicate that most of the toxic constituents found in municipal leachates are moderately to highly attenuated by passage through laboratory columns that contain relatively low percentages of clay minerals. If the assumption is granted that the bathtub effect is an undesirable feature of clay liners, then it follows that it is

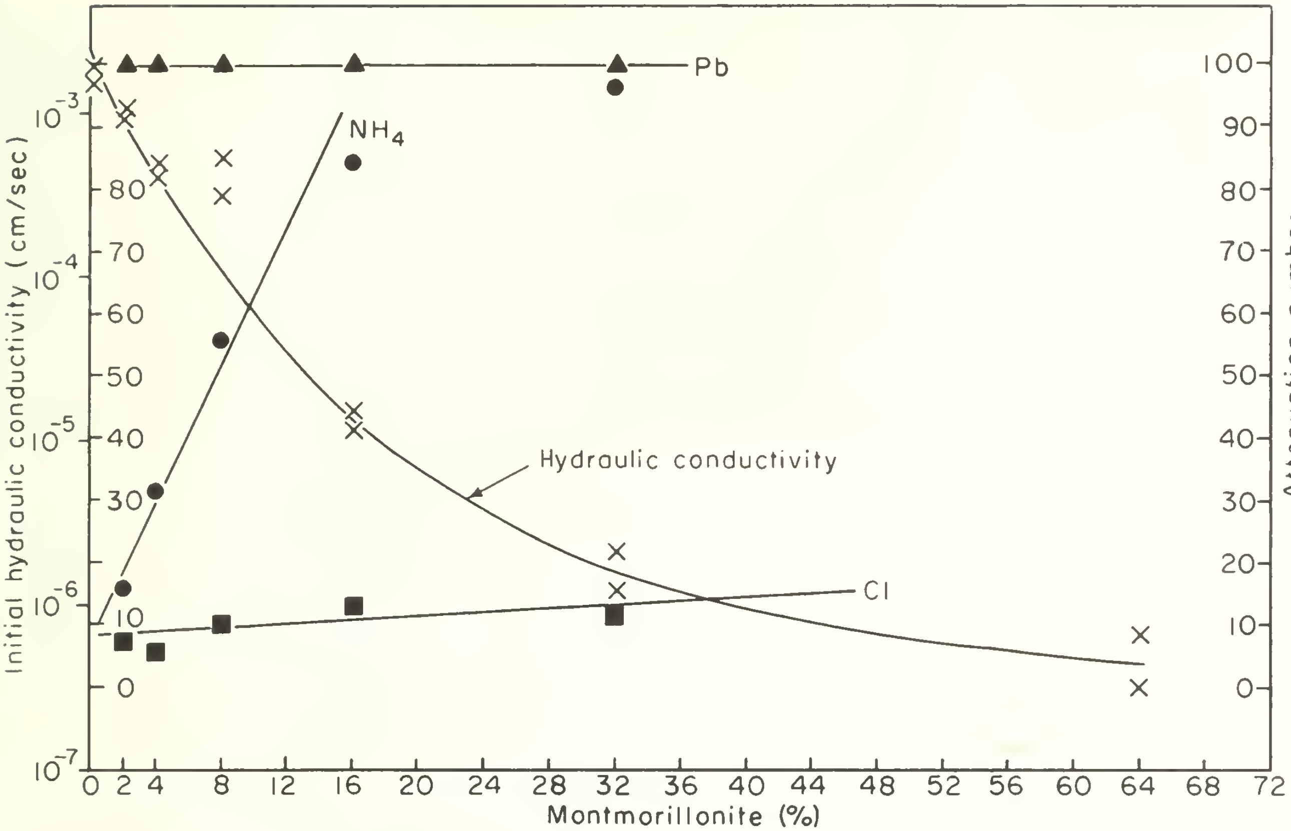

Fig. 12 - "Optimal" montmorillonite percentages for attenuation of Pb^{++}, NH_4^+, and Cl^-

desirable to determine the point of "optimal" attenuation, i.e., the percentage of clay in a liner material that gives the maximum attenuation and the maximum hydraulic conductivity. The "optimal" percentage of montmorillonite determined for Cl, NH_4, and Pb is shown on a dual-scaled graph in figure 12, on which the initial hydraulic conductivity of the montmorillonite columns (table 3) is plotted as a function of the percentage of montmorillonite. On the opposite scale is the attenuation number for the chemical constituent, also plotted as a function of the percentage of montmorillonite. The attenuation number scale runs from 0 at the point of minimum hydraulic conductivity to 100 at the point of maximum hydraulic conductivity. The point where the attenuation curve and the hydraulic conductivity curve cross is considered the "optimal" percentage of montmorillonite that gives the optimum balance of attenuation and permeability.

For the metals (Pb is used here as an example), even small amounts of clay resulted in almost total removal. The metals, even though toxic, represent a minimal pollution hazard in municipal leachates because they are attenuated very strongly. Therefore, they can usually be dismissed from consideration as far as determination of the optimal clay liner for a given leachate is concerned. At the other extreme are the relatively noninteracting constituents represented by Cl. Chloride, as shown in figure 12, is relatively unattenuated by even large amounts of clay. The figure indicates that relatively impermeable clay liners would be necessary to prevent chloride migration. Because the chloride ion is nontoxic, it ranks low in the pollution hazard index (table 6). In view of the problems associated with the bathtub effect, it seems unwise to design clay liners for optimum chloride attenuation. Rather, it seems prudent to design clay liners for optimum attenuation of the most hazardous constituents found in a particular leachate. For the Du Page leachate used in this study, the pollution hazard index ranks NH_4 as 30 times more of a pollution hazard than any other constituent. A liner designed to contain Du Page leachate, therefore, should provide optimal attenuation of NH_4 and should also attenuate all the other constituents to relatively safe levels to keep pollution of the ground water adjacent to the landfill site to a minimum.

For NH_4 (fig. 12) the optimal attenuation was achieved by approximately 10 percent montmorillonite. If the curve is extrapolated, it is apparent that 18 to 20 percent montmorillonite would remove nearly all of the NH_4 from the leachate. The ratio of the optimal percentage and the percentage necessary for nearly total removal indicates that if the 10 percent liner is doubled in thickness, from the 40 cm used in this study to 80 cm, it will contain enough montmorillonite to give nearly total removal of the NH_4 in 10 pore volumes of leachate and still retain the relatively high hydraulic conductivity of 6×10^{-5} cm/sec.

Predicting Pollutant Migration

The thickness of various mixtures of sand and clay, represented by the total cation exchange capacity (CEC), needed to achieve total attenuation of selected relatively mobile ions was calculated (table 7). The removal efficiency of the clay will differ with the leachate, depending upon relative ion strength. The efficiencies used in table 7 are based on the Du Page leachate used in this study. The Du Page leachate concentrations are given in parentheses under the average concentration value reported by the U.S. EPA (1974). Increasing cation exchange capacity generally reflects increasing clay content. Thus, a thick liner with a high hydraulic conductivity and low CEC may be the optimal liner for attenuation.

Determining the release rate of nonattenuated or poorly attenuated contaminants from the clay liner (natural or man-made) to surface waters or ground-water aquifers is a necessary step for good landfill design. A decision must be made as to which ions should be totally attenuated and which could be eventually released to the environment. The chloride ion, which moves out of the landfill essentially unattenuated, is the most obvious example of the latter type.

The calculation of the release rate of fluid from the bottom and sides of a landfill and the flow path it will take is a complex task. Several models, existing or under development, use a high-speed digital computer to predict the rate and path of fluids from a landfill (*e.g.*, Elzy et al., 1974). These models are quite accurate and will provide good estimates of the parameters desired. They are, of course, dependent upon the accuracy of the input physical data—infiltration rates, hydraulic conductivities, and geologic descriptions.

TABLE 7—ESTIMATED LANDFILL LINER THICKNESS NECESSARY FOR ATTENUATION OF SOME LEACHATE CONSTITUENTS PER CUBIC METER OF REFUSE DURING A 20-YEAR FILL LIFE*

	Initial concentration†		Thickness of liner					
			CEC 10		CEC 20		CEC 30	
Constituent	Average (ppm)	Maximum (ppm)	Average (cm)	Maximum (cm)	Average (cm)	Maximum (cm)	Average (cm)	Maximum (cm)
NH_4	379 (830)	1,106	32	92	16	46	11	31
Na	755 (740)	7,700	118	1,208	59	604	39	403
K	763 (530)	3,770	51	252	26	126	17	84
Mg	1,609 (240)	15,600	226	2,191	113	1,096	75	730

* Assumptions: Bulk density = 1.8 b/cc; 100 liters of leachate generated per m^3 of refuse per year; initial concentration decreases linearly to zero at 20 years; removal efficiencies for each constituent were estimated by using the average values given in table 4.

† Concentrations taken from the 20 leachate analyses reported by EPA (1974); those in parenthesis (830) are the values of old Du Page landfill leachate used in this study.

Preliminary estimates of leakage can also be made by simply using Darcy's equation, as suggested by Hughes, Landon, and Farvolden (1971):

$$Q = KA \frac{dH}{dL}$$

where Q = flow rate in cm^3/sec,
A = area of the landfill in cm^2,
dL = thickness of the liner in cm, and
dH = head of water across the liner, in cm.

This equation has some of the same limitations as the computer-predicted models—its success depends on the accuracy of the hydraulic conductivities and the hydraulic gradients provided. Either estimated or measured values of hydraulic conductivity can be used. However, the presence of a landfill generally changes the hydraulic gradient. In addition, the gradient will differ with changing hydraulic conductivities. Hughes, Landon, and Farvolden (1971) observed gradients as high as 1 cm/cm in glacial till with a hydraulic conductivity about 4×10^{-7} cm/sec, and found a 0.02 cm/cm gradient in dirty surficial sand with a hydraulic conductivity 1×10^{-3} cm/sec. Therefore, knowledge of local materials would permit an estimation of the value of $\frac{dH}{dL}$.

The calculated leakage must then be compared in volume to the receiving waters. If a surface water body is receiving the pollutant discharge, the calculation is relatively straightforward. For instance, Hughes, Landon, and Farvolden (1971) calculated that the Elgin landfill, located in highly permeable gravel, contributed 0.30 parts per million dissolved solids to the Fox River.

TABLE 8—INCREASE IN SALINITY OF AN AQUIFER OR SMALL STREAM CAUSED BY LANDFILL LEACHATE*

Hydraulic conductivity of liner (cm/sec)	Gradient (cm/cm)	Increase in aquifer salinity (ppm)	Increase in stream salinity (ppm)
1×10^{-8}	1/1	0.8	0.002
1×10^{-6}	1/10	7.7	0.02
1×10^{-4}	1/100	77.	0.2
1×10^{-2}	1/1000	769.	2.0

* Assumptions:
1) Hydraulic conductivity of the aquifer is 1×10^{-2} cm/sec and its gradient is 1/1000 cm/cm.
2) 10^4 square meters of refuse.
3) Aquifer 30 meters thick.
4) Leachate salinity 2000 ppm (Hughes, Landon, and Farvolden, 1971).
5) Stream discharge 1 m^3/sec.

Leakage to aquifers is more difficult, and the computer models have considerable advantage. However, the volume of water passing below the landfill can be calculated in a way similar to that in which the leakage was calculated, where A in the Darcy equation becomes the cross sectional area of the aquifer. However, ground-water flow is laminar, and dispersion becomes the only mechanism for dilution into the total volume of water. The calculation therefore represents a total value for the receiving aquifer and not a spot value. Nevertheless, these two simple calculations may furnish needed preliminary information before the more detailed hydrogeologic analyses are made.

Table 8 shows some representative estimates of increased ion concentration in some surface water streams and aquifers. The table was calculated assuming an aquifer 30 meters thick with a hydraulic conductivity of 1×10^{-2} cm/sec and a fairly small stream with a discharge of 1 m^3/sec. The salinity of the discharge is assumed to be 2000 ppm, like that found at the Elgin landfill by Hughes, Landon, and Farvolden (1971).

The results of this study raise some basic questions as to landfill design and monitoring. They indicate that use of hydraulic conductivity information and the pollution hazard rating for a given leachate or waste stream can allow an approach to landfill design different from the prevalent "containment" policy. These data suggest that over-all pollution could be reduced by designing landfill liners that have higher permeability and can selectively attenuate the most toxic pollutants from the leachate, leaving the ground waters to dilute the nontoxic components, which can be tolerated at much higher concentrations without deleterious effects. Such liners would allow landfills to stabilize more quickly and make it possible for the land to be used for other purposes much sooner than is possible now with the use of liners that consider only containment.

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